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# STUDY PROGRAM TO DEVELOP AND EVALUATE DIE AND CONTAINER MATERIALS FOR THE GROWTH OF SILICON RIBBONS

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QUARTERLY REPORT NO. 5

JANUARY 1979



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Pasadena, California 91103

EAGLE  PITCHER

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## SUMMARY

Die and container material development efforts under the current program are shared among three organizations. Miami Research Laboratories (MRL) - ceramic process development and overall program management, University of Missouri-Rolla (UMR) - silicon sessile drop studies with characterization of reaction products and emphasis on atmospheric effects, Chemetal Corporation, Pacoima, California - special coatings to be applied to test coupons, die shapes, and containers provided by MRL and tested/characterized by UMR.

The completion of a major hardware delivery milestone was accomplished with the delivery of three CNTD  $\text{Si}_3\text{N}_4$  coated hot pressed  $\text{Si}_3\text{N}_4$  crucibles to JPL. A limited characterization of the coating was performed at MRL prior to delivery. The coatings were fine grained  $\alpha - \text{Si}_3\text{N}_4$ . It has been determined that a two piece die design will be required.

At UMR the importance of the role of oxygen in influencing the attack of the CNTD materials by molten silicon has been demonstrated. The stability is greatly enhanced by maintaining the oxygen partial pressure near or below the  $\text{Si} + \text{O}_2 = \text{SiO}_2$  equilibrium.

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## 1. INTRODUCTION

The current program is a cooperative effort among three facilities to attack the die and container materials problems of the Low Cost Silicon Array Project. Miami Research Laboratories (MRL) provides overall project management as well as die and container fabrication engineering and characterization. Chemetal Corporation (Pacoima, California) applies ceramic coatings to substrates for testing and later to die and container shapes made by MRL using the proprietary "CNTD" (Controlled Nucleation by Thermochemical Decomposition) process. University of Missouri-Rolla (UMR) personnel perform sessile drop experiments on coated substrates made by MRL and Chemetal. They are investigating the effects of oxygen partial pressure and characterizing the reactions using Auger spectroscopy, ESCA and other techniques.

The goal of the program is to develop successful die and container materials for handling liquid silicon while it is being formed into photovoltaic cell material. The goal is being pursued by exploring various material configurations for their reactivity with molten silicon. The studies of the effects of oxygen partial pressure are yielding valuable information concerning the role of oxygen in the interaction of molten silicon with these unique materials. Successful experimental configurations have been selected for fabrication of crucibles and dies.

The systems selected for fabrication into hardware delivery items (ie. crucibles and dies) are CNTD  $\text{Si}_3\text{N}_4$  coated on a hot pressed  $\text{Si}_3\text{N}_4$  body with 4wt% MgO as a pressing aid and CNTD SiC coated on a hot pressed SiC body with 1wt% B as a pressing aid.

## 2. MIAMI RESEARCH LABORATORY EFFORTS

Miami Research Laboratory activities this period included the hot pressing of crucibles and die blanks from SiC w/lwt% B, the grinding of die blanks to the required die geometry for coating, and the characterization of the CNTD  $\text{Si}_3\text{N}_4$  coated crucibles prior to delivery to JPL.

### 2.1 SILICON CARBIDE CRUCIBLE AND DIE BLANK HOT PRESSING

The SiC crucibles were hot pressed from powder lots PP-26 B and PP-26 C (SiC w/lwt% B, both lots) to the nominal dimensions of 2 1/2" O.D. x 2" I.D. x 1 1/2" deep x 1 3/4" overall height. The outside bottom of the crucibles was the frustum of a cone with a  $60^{\circ}$  angle of divergence at the projected tip. The cone was truncated such that a stable base was provided for the crucible. The reasons for selection of this geometry were delineated in the fourth quarterly report for this program. The crucible hot pressing temperature was  $2300$  to  $2330^{\circ}\text{C}$  and the applied pressure was  $2400$  to  $2500 \text{ lb/in}^2$  (calculated from the pressing load in pounds divided by the total area defined by the crucible O.D.). Total run time was from 55 to 75 minutes with 15 to 20 minutes of that time utilized in increasing temperature and pressure. The final densities ranged from 85.5 to 86% of theoretical.

The SiC die blanks were hot pressed from powder lot PP-26 B (SiC w/lwt% B) at  $2300^{\circ}\text{C}$ ,  $3725 \text{ lb/in}^2$  and total run times of 70 to 90 minutes. Approximately 15 minutes of that time was utilized in increasing temperature and pressure. Final densities ranged from 87.4 to 93.9% of theoretical with the average falling at 90.1% T.D.

### 2.2 DIE GRINDING

The Program Plan was based upon a reasonable assumption of success in grinding and coating a one piece die of a design suggested

by JPL. The die design suggested by JPL was modified by changing the slot width from 0.015" to 0.025" to allow for a 0.005" thick coating of CNTD material on each internal surface of the slot. The original design was rather difficult to fabricate from a hard, brittle material such as ceramic, however, pieces were produced in spite of an alarming mortality rate.

Base upon the difficulty of grinding a one piece die and the subsequent difficulty incurred at Chemetal in applying an adequate CNTD coating to the internal surfaces (see section 4) the decision was made to utilize a two piece die design. The two piece die was based upon a JPL suggested design. It was modified, however, to include thicker sections to decrease grinding mortality. The modified two piece design was developed through a careful consideration of the often conflicting requirements of reasonable degree of grinding difficulty (ie. probability of surviving grinding), suitable geometry for the coating process, and suitable geometry for crystal growth. The probability of success with the two piece die design is greatly enhanced by the incorporation of experience in working with the one piece design.

### 2.3 SILICON NITRIDE CRUCIBLE COATING CHARACTERIZATION

Three CNTD  $\text{Si}_3\text{N}_4$  coated crucibles of hot pressed  $\text{Si}_3\text{N}_4$  w/4wt% MgO were completed during this period (see section 4). The CNTD  $\text{Si}_3\text{N}_4$  coating was transparent and approximately 0.005" thick. The crucibles were coated in the "as hot pressed" surface condition (ie. no internal or external grinding). The grinding was omitted in order to provide parts prototypic of what one could hope to manufacture at a reasonable cost. The CNTD  $\text{Si}_3\text{N}_4$  coating uniformly covered the irregularities in the as-pressed part.

Examination of the CNTD surface with a stereozoom microscope

at relatively low magnifications revealed a fine grain size with an occasional large crystallite rising out of the surface to a height estimated to be a few hundred microns (less than 1 mm). X-ray diffraction analysis of a small chip sawed from the top edge of one of the crucibles showed the coating to be crystalline  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>. The crystalline nature of the coating is confirmed by the SEM photomicrograph shown in Figure 1. The area shown is typical with regard to crystallite size in the as deposited coating.



Figure 1. SEM Photomicrograph of CNTD  $\text{Si}_3\text{N}_4$  Coating, Crucible HP-453.  
1500X, as deposited.

### 3. UMR EFFORTS

The principal thrust at U.M.R. this period has been to continue the investigation of oxygen partial pressure effects on the interaction between molten silicon and various CNTD coated ceramic materials and the evaluation of the suitability of these candidates for the die and container materials in the LSA project. Silicon sessile drop measurements have been pursued on the CNTD coated specimens of AlN, SiC and  $\text{Si}_3\text{N}_4$  to elucidate the effects of oxygen partial pressure. Some sessile drop tests have also been performed on uncoated hot pressed  $\text{Si}_3\text{N}_4$  substrates to compliment the understanding of the wetting phenomena of molten silicon on  $\text{Si}_3\text{N}_4$  material. Characterization techniques of SEM, optical microscopy and AES are employed in the post sessile drop test specimens to evaluate the severity of molten silicon's attack of these materials. The post test separation of CNTD coated layers from the hot pressed substrates of  $\text{Si}_3\text{N}_4$  and SiC has been investigated, as well, through the employment of SEM on the separated CNTD layers.

#### 3.1 SILICON SESSILE DROP TEST

Sessile drop tests are conducted in a sealed alumina tube under a flowing gas buffer to precisely control the oxygen partial pressure. The alumina tube runs through the hot zone of a sealed chamber of a water cooled molybdenum resistance furnace. Pyrex, ultra high vacuum type viewports, sealed at each end of the alumina tube allow for simultaneous temperature and silicon sessile drop contact angle measurements to be made. An Yttria doped thoria cell is employed to determine the oxygen partial pressure over the sessile drop substrate test sets. A complete arrangement for the test is schematically illustrated in Figure 2. The oxide cell has been described in quarterly report no. 4.

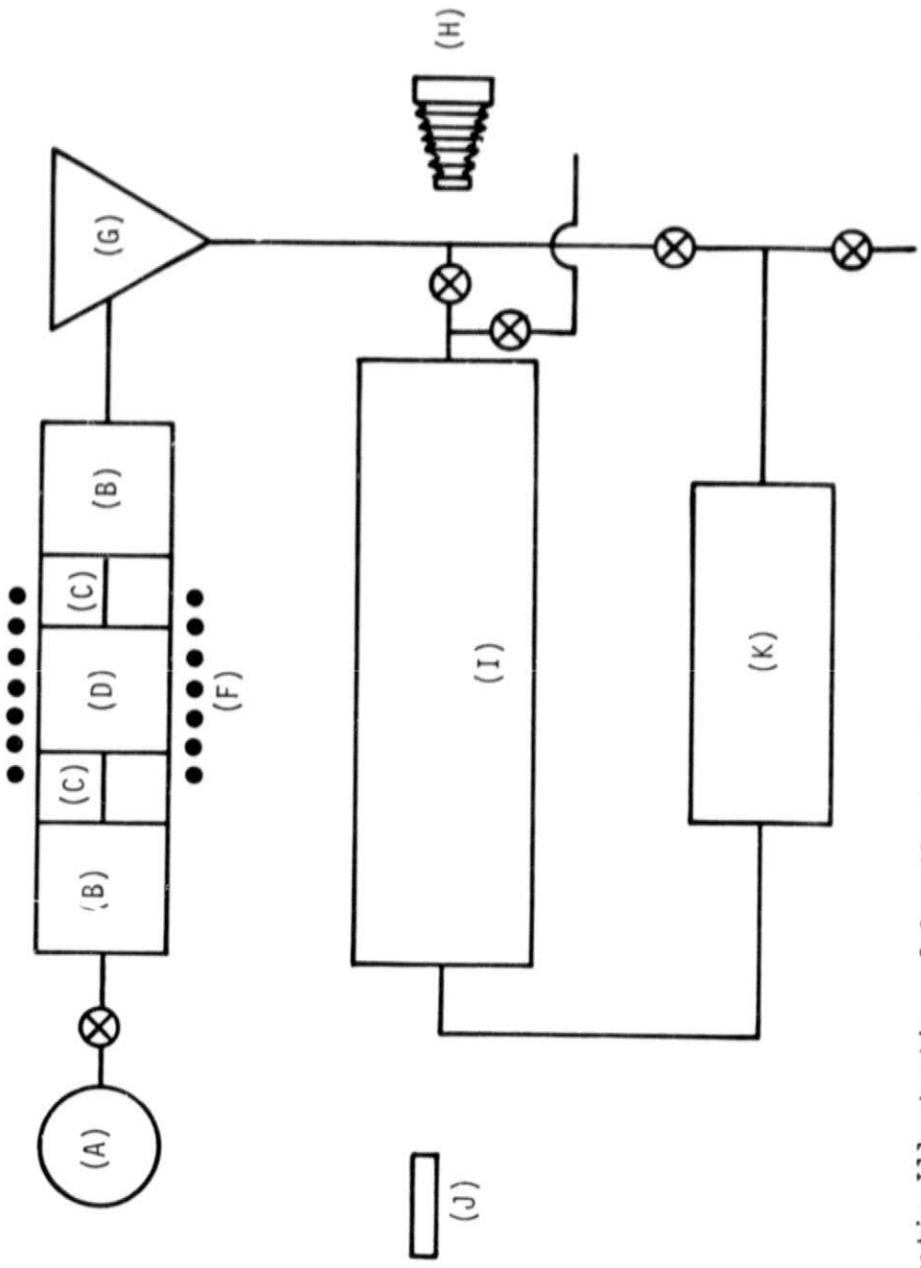


Figure 2. Schematic Illustration of Sessile Drop Experiment Under Precisely Defined Oxygen Partial Pressure  
 (A) Hydrogen gas, (B) Platinized asbestos, (C)  $\text{Al}_2\text{O}_3$  separator, (D) Titanium powder, (E) Heating element, (G) Cold-trap-chiller, (H) Camera, (I) Sessile drop test furnace, (J) Optical pyrometer, (K) Oxide cell

Photographs are taken during the sessile drop experiment at predetermined intervals. Contact angles are measured on the projected image of the negative. A typical photograph of the sessile drop test is presented in Figure 3. Horizontal alignment of the silicon/specimen set inside the alumina tube is necessary to insure the accuracy of the contact angle measurement.

### 3.1.1 Wetting Phenomena of CNTD Coated $\text{Si}_3\text{N}_4$ by Silicon

Silicon sessile drop tests on the polished surface of CNTD coated  $\text{Si}_3\text{N}_4$  are performed under various conditions to investigate the effects of oxygen partial pressure and temperature on the interaction between molten silicon and CNTD coated  $\text{Si}_3\text{N}_4$ .

Photographs of sessile drop experiments at the initial stage for two different oxygen partial pressures are presented in Figure 4. The oxygen partial pressure is found to have a large effect on the wetting phenomena at the initial stage ( $t=0$ ). Above  $10^{-18}$  atm  $P_{\text{O}_2}$  the initial liquid drop interface is not perfectly smooth. As  $P_{\text{O}_2}$  is lowered to  $8.1 \times 10^{-19}$  atm, the initial contact angle is  $65^\circ$  and the surface still appears somewhat rough suggesting residual oxide on the surface of the silicon drop. Further lowering the  $P_{\text{O}_2}$  value to  $3.3 \times 10^{-19}$  atm, close to the equilibrium oxygen partial pressure of  $\sim 1.8 \times 10^{-19}$  atm for  $\text{SiO}_2$  - Si system at  $1420^\circ\text{C}$ , the initial contact angle is  $64^\circ$  with no residual oxide in sight and the interface appears perfectly smooth.

Previous sessile drop measurements in the literature and in this work have been limited to relatively short time runs of the order of one hour. Longer time runs were considered more meaningful because short time measurements are not only less reproducible but do not represent data of significance for application in actual longer use times, ie. melting and forming silicon into sheets or ribbons.

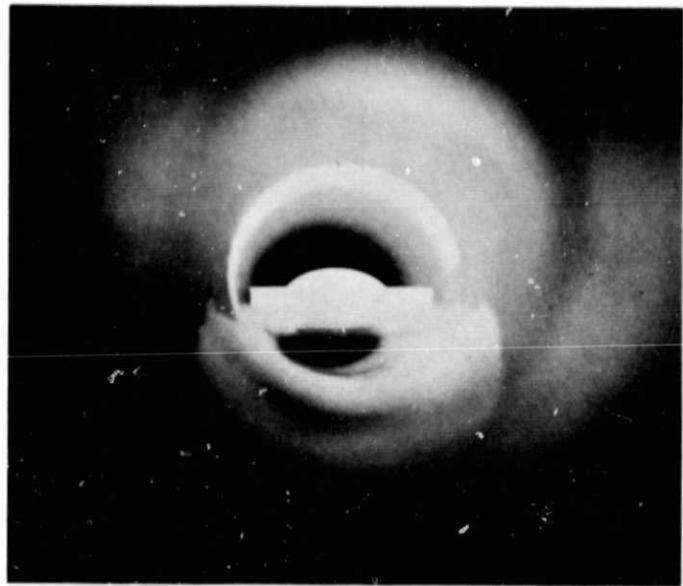
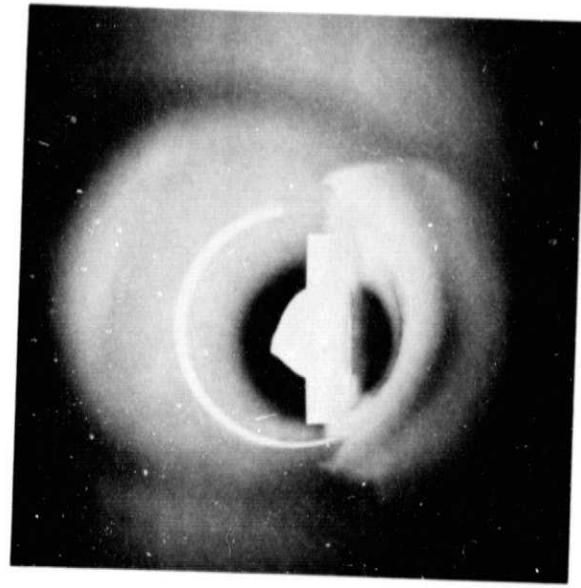
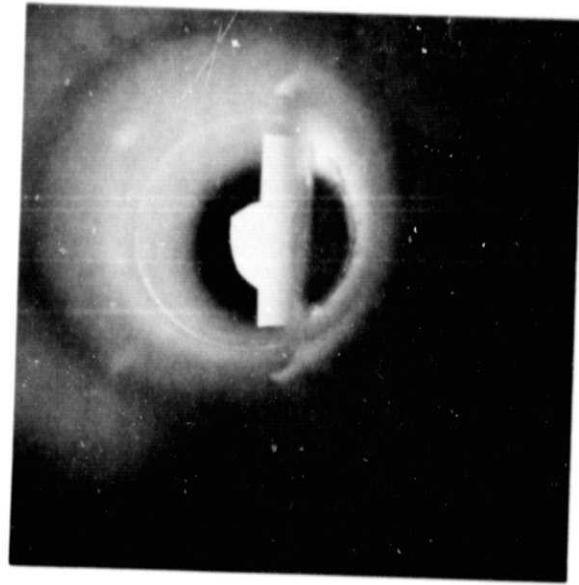


Figure 3. Typical Photograph for Silicon Sessile Drop Test.



a)



b)

Figure 4. Initial Stage ( $t=0$ ) Sessile Drop  $1420^{\circ}\text{C}$  and Varying  $P_{\text{O}_2}$  on CNTD  $\text{Si}_3\text{N}_4$

- a)  $P_{\text{O}_2} = 8.1 \times 10^{-19} \text{ atm}$ , silicon drop surface not sharp and smooth.
- b)  $P_{\text{O}_2} = 3.3 \times 10^{-19} \text{ atm}$ , silicon drop surface sharp and smooth.

Ten hour histories of the silicon contact angle tested under different atmospheres were therefore taken with oxygen partial pressures of  $2.3 \times 10^{-18}$ ,  $1.4 \times 10^{-18}$  and  $3.3 \times 10^{-19}$  atm and are presented in Figure 5 to illustrate the effect of oxygen partial pressure and time on the wetting of CNTD coated  $\text{Si}_3\text{N}_4$  by molten silicon. The initial rates of decreasing contact angles are found to be decreasing very fast with time and then more slowly and stabilizing in the  $P_{O_2}$  ambients of  $1.4 \times 10^{-18}$  atm and  $3.3 \times 10^{-19}$  atm. The contact angle measured in the highest  $P_{O_2}$  shown in Figure 4 ( $2.3 \times 10^{-18}$ ) shows the least tendency toward stabilization. It is apparent that the oxygen partial pressure has great influence on the decreasing contact angle rate. Change in contact angle with time is generally thought to be a result of the interaction among phases. The results suggest that decreasing the oxygen partial pressure below the  $\text{SiO}_2$ -Si equilibrium oxygen partial pressure significantly suppresses the interaction between molten silicon and CNTD coated  $\text{Si}_3\text{N}_4$ , since the contact angle apparently becomes virtually constant. Further work in the low  $P_{O_2}$  range is necessary to complete the understanding of oxygen partial pressure effect.

Figure 6 shows the sessile drop test specimens used to generate the data presented in Figure 5. The formation of oxidation products is observed to decrease with decreasing  $P_{O_2}$  value in the sequence of Figure 6-a to 6-c, which is as expected. The specimen shown in Figure 6-a was the object of an experiment to gather information concerning the mechanism of etching of the CNTD  $\text{Si}_3\text{N}_4$  surface. Prior to the sessile drop run the specimen was sawed in half, then broken, thereby providing sections I.II, III, and IV. The sessile drop run was performed at  $1420^{\circ}\text{C}$  at a  $P_{O_2}$  of  $2.3 \times 10^{-18}$  atm. The experiment was set up with section I placed in the normal position with two small silicon cubes resting upon it.

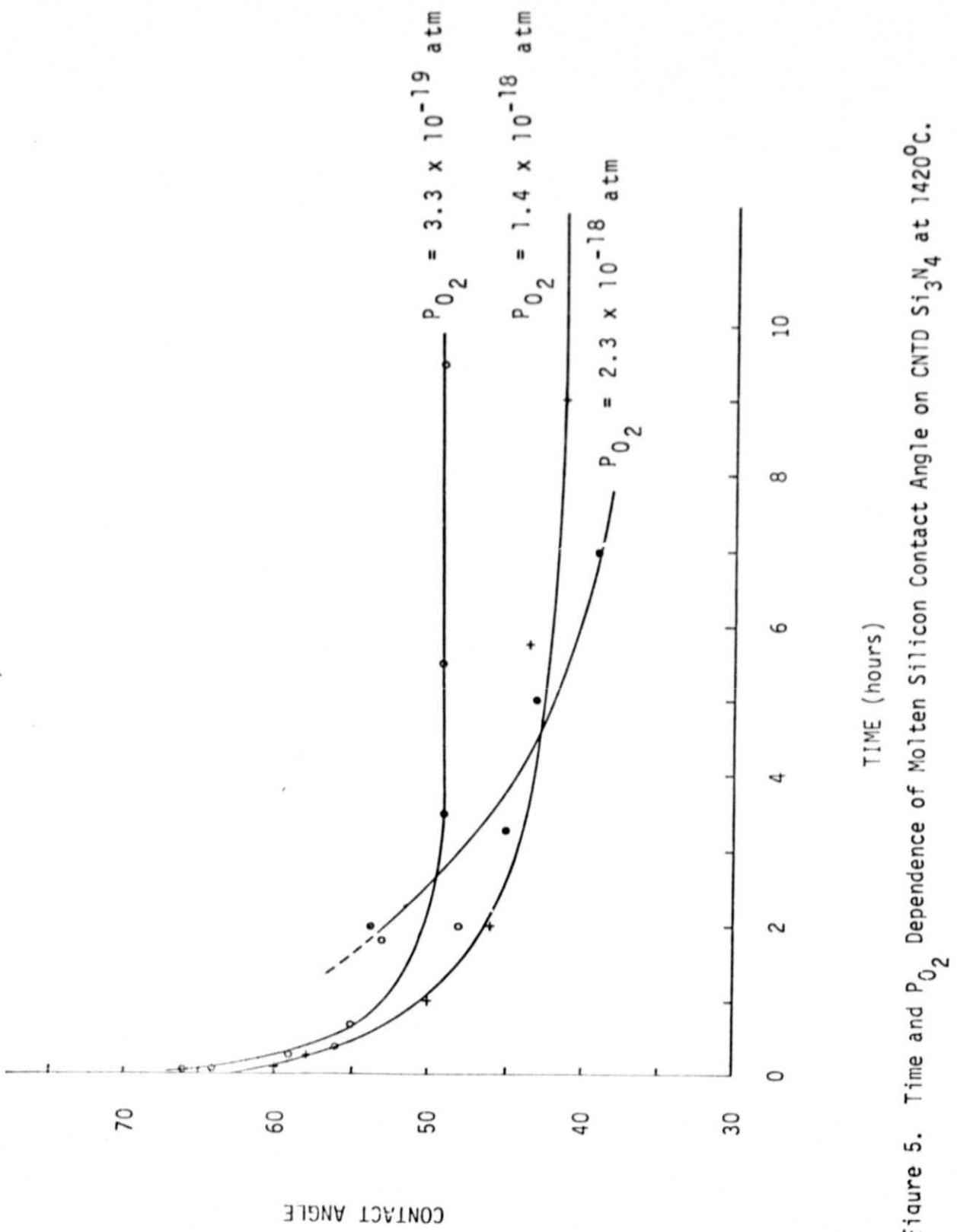
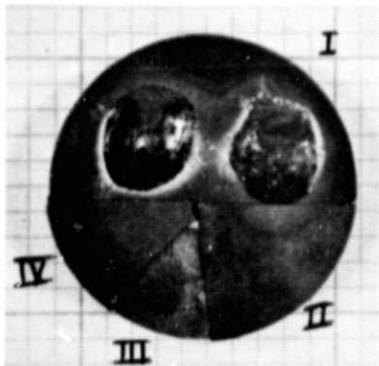
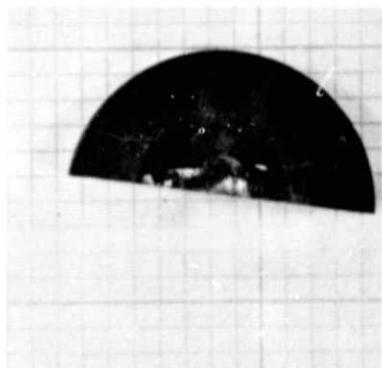


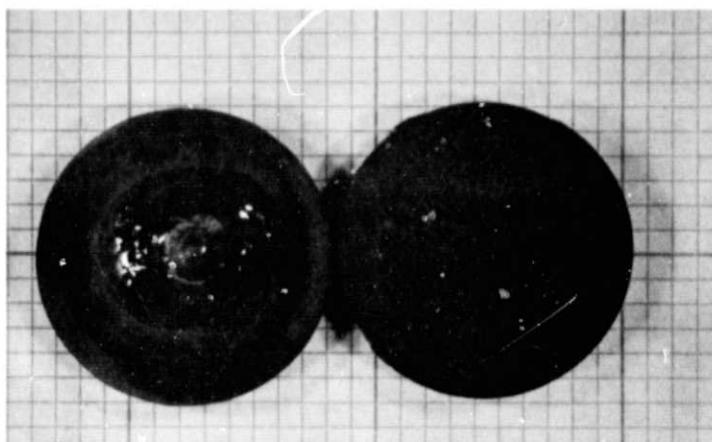
Figure 5. Time and  $P_{O_2}$  Dependence of Molten Silicon Contact Angle on CNTD  $\text{Si}_3\text{N}_4$  at  $1420^{\circ}\text{C}$ .



a)



b)



c)

Figure 6. Sessile Drop Test Specimens of CNTD Si<sub>3</sub>N<sub>4</sub> From Which Figure 5 Data was Obtained.

a)  $P_{O_2} = 2.3 \times 10^{-18}$  atm

b)  $P_{O_2} = 1.4 \times 10^{-18}$  atm

c)  $P_{O_2} = 3.3 \times 10^{-19}$  atm

See text for full explanation.

Section II was placed adjacent to Section I, oriented as the specimen existed prior to cutting. Due to the cutting, however, the CNTD surface was interrupted, providing a discontinuity for surface diffusion or micro-wetting. Section III was placed in the alumina muffle in the same temperature regime but upstream (with respect to gas flow) from the section I/II set. Section IV was left in as-received condition for comparison. Figure 6-a shows that the pattern of etching of the CNTD  $\text{Si}_3\text{N}_4$  surface proceeds beyond the surface interruption, indicating that in this  $P_{\text{O}_2}$  range ( $2.3 \times 10^{-18}$  atm) a vapor phase mechanism is at work.

The etching of the CNTD coating near the sessile drop may take on a network type appearance. Figure 6-c shows that these patterns resemble the network patterns on the polished CNTD  $\text{Si}_3\text{N}_4$  surfaces in the as-received condition. The patterns are believed to result from preferential etching of the CNTD structure along the crack-like networks described in previous reports.

A higher temperature sessile drop test on CNTD coated  $\text{Si}_3\text{N}_4$  has been conducted at  $1490 \pm 10^\circ\text{C}$  under an oxygen partial pressure near the equilibrium value for the Si-SiO<sub>2</sub> system at this temperature to investigate the temperature effect on the wetting phenomena of this material by molten silicon. It can be seen on Figure 7, that the contact angle stabilizes at a constant value of  $50^\circ$  in a shorter time period at this temperature than at  $1420^\circ\text{C}$ . This result is consistent with the higher mobility at higher temperatures. It also suggests that the final stabilized contact angle is insensitive to temperature as long as the  $P_{\text{O}_2}$  value in the atmosphere is close to or below the equilibrium  $P_{\text{O}_2}$  of the Si-SiO<sub>2</sub> system.

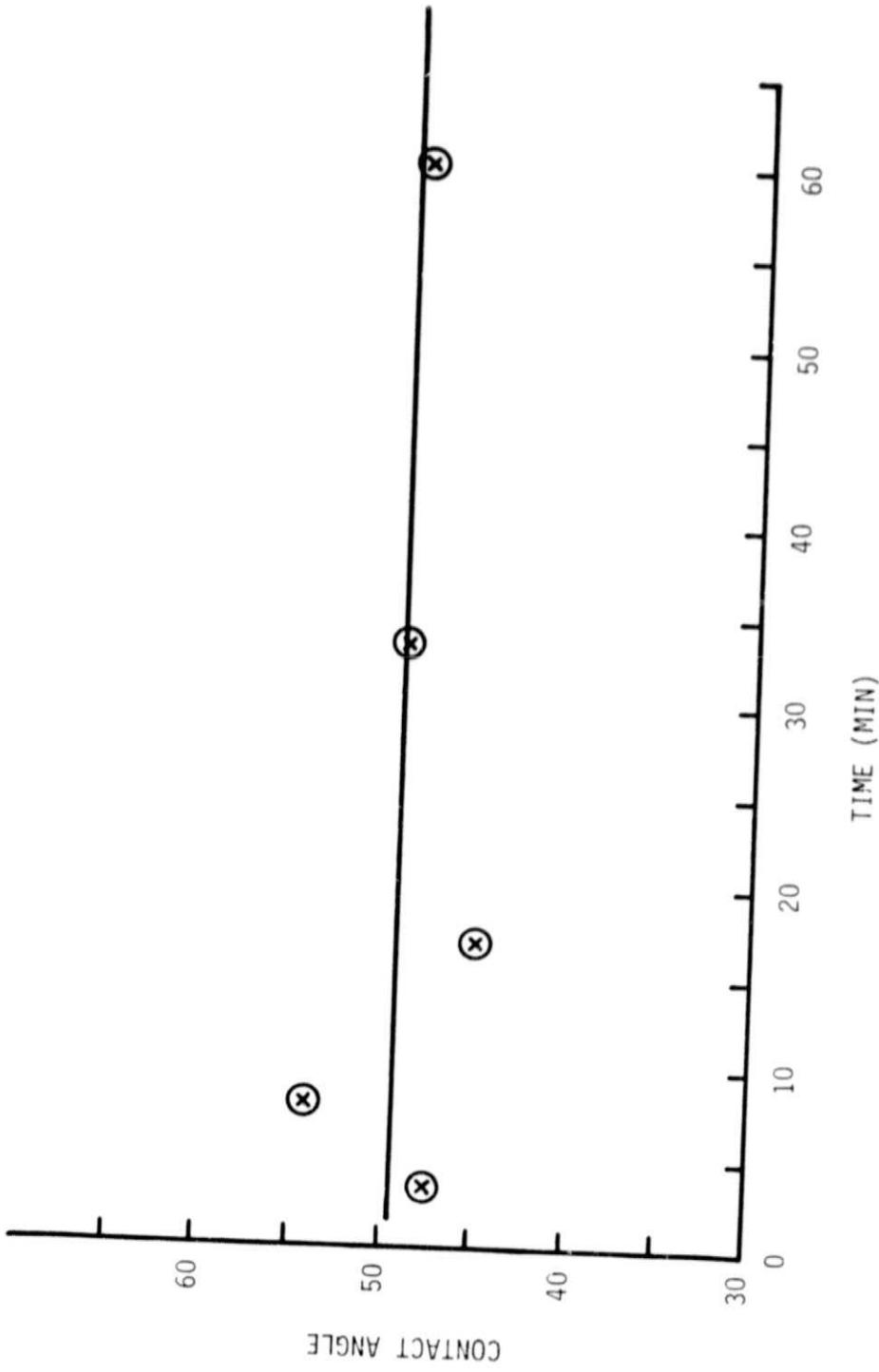


Figure 7. Contact Angle as a Function of Time for CNTD  $\text{Si}_3\text{N}_4$  at  $2 \times 10^{-18}$  atm  $P_{\text{O}_2}$  and  $1490^{\circ}\text{C}$ .

Note: t=0 proceeded by 1/2 hour heat up.

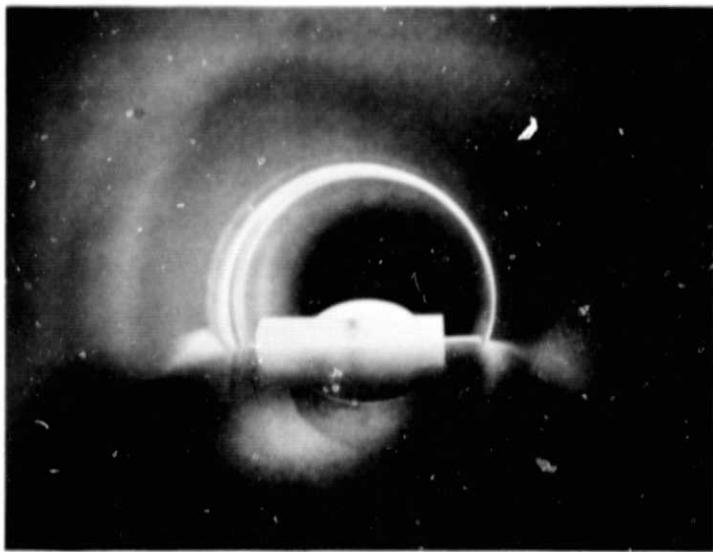
### 3.1.2 Wetting of Uncoated $\text{Si}_3\text{N}_4$ by Molten Silicon

Uncoated hot pressed  $\text{Si}_3\text{N}_4$  w/4wt% MgO ( $\sim 90\%$  T.D.) substrates were employed in our silicon sessile drop test program to 1) supplement our understanding of oxygen partial pressure effect and 2) because of the limited number of coated specimens available. An additional result is to contrast the difference in performance of the CNTD coated specimens with that of the uncoated ones.

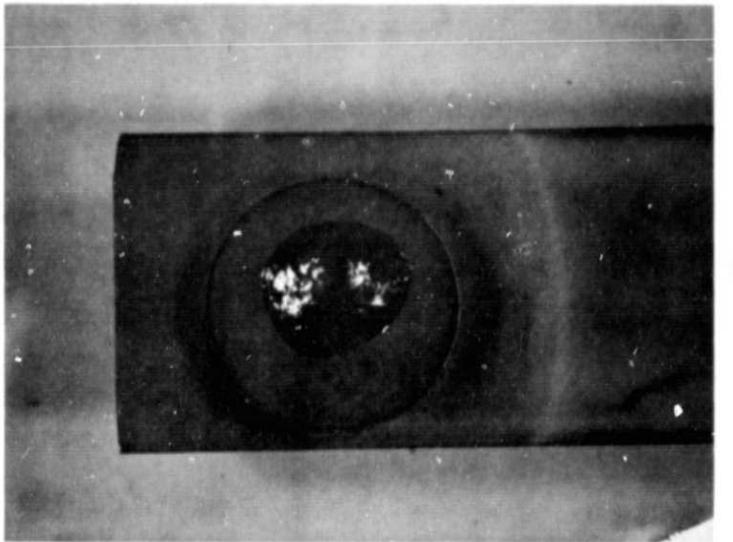
Silicon sessile drops on uncoated hot pressed specimens in many cases exhibit variances in contact angle with position along with periphery. These variances may result in significant differences in contact angle measurements from one side of the drop test photograph to the other. Typically, an inequality between the contact angle measurements on each side of the silicon drop coincided with the formation of a satellite drop of molten silicon on the cylindrical sidewall of the substrate during the drop testing period.

An *in situ* sessile drop profile photograph and a post test top view photograph of this type of occurrence are shown in Figure 8. The satellite drop is seen on the left edge of the disc in Figure 8-a and at the seven to eight o'clock position in Figure 8-b. Micro-flow or excessive micro-wetting of molten silicon on the surface of the uncoated  $\text{Si}_3\text{N}_4$  is believed to be the reason for the difference in the two observed contact angles. The limited data on these uncoated substrates seems to suggest that micro-flow of molten silicon may be suppressed by the presence of oxygen. At lower oxygen partial pressures, the micro-flow of silicon appears to be more pronounced.

The high silicon contact angle ( $\sim 72^\circ$ ) measured and the absence of silicon micro-flow on the uncoated  $\text{Si}_3\text{N}_4$  substrate in a relatively high oxygen partial pressure ( $3 \times 10^{-17}$  atm) ambient suggests



a) - During test



b) - Post test

Figure 8. Silicon Sessile Drop Test on Uncoated  $\text{Si}_3\text{N}_4$  w/4wt% MgO  
at  $1420^{\circ}\text{C}$ , 12 hrs.,  $3 \times 10^{-17}$  atm  $\text{P}_{\text{O}_2}$ .

Note satellite drop in - a) left edge and b) 7:00 o'clock.

the formation of a very thin oxide layer on top of this specimen. Lowering the oxygen partial pressure is necessary to remove the masking effect of the presence of an oxide layer and to yield the valuable information about molten silicon/Si<sub>3</sub>N<sub>4</sub> interaction.

### 3.1.3 Wetting of CNTD Coated SiC of Molten Silicon

Due to the paucity of CNTD coated SiC specimens, only one sessile drop test has been performed on CNTD coated SiC during this reporting period. The silicon contact angle on CNTD coated SiC tested at a temperature of 1420  $\pm$  5° C and under an atmosphere in the range of the equilibrium oxygen partial for SiO<sub>2</sub>-Si system, is presented in Figure 9 as a function of time where it is compared with similar data for CNTD AlN and Si<sub>3</sub>N<sub>4</sub>. Initial contact angle is found to be 40° which is close to the values reported for molten silicon and SiC system elsewhere. Near the equilibrium oxygen partial pressure the contact angle, however, decreases with time and stabilizes at a value of 25°. Further work is necessary to reveal the detailed oxygen partial pressure effects of the interaction between liquid silicon and CNTD coated SiC.

### 3.1.4 Wetting of CNTD Coated AlN by Molten Silicon

Silicon sessile drop tests on the polished surface of CNTD AlN were conducted at different temperatures, time and oxygen partial pressures. In contrast to the CNTD Si<sub>3</sub>N<sub>4</sub> and CNTD SiC coatings the contact angles of molten silicon/CNTD AlN systems near the equilibrium oxygen pressure (Si + O<sub>2</sub>  $\rightleftharpoons$  SiO<sub>2</sub>) continuously decrease as shown by the example on Figure 9. This suggests that AlN is the most reactive of the three CNTD coatings with molten silicon at an oxygen partial pressure of  $\sim 10^{-19}$  atmospheres. During the silicon sessile drop test on CNTD AlN coated specimens a fibrous deposit is generally found on the coated substrate circumscribing the drop as shown in Figure 10-C.

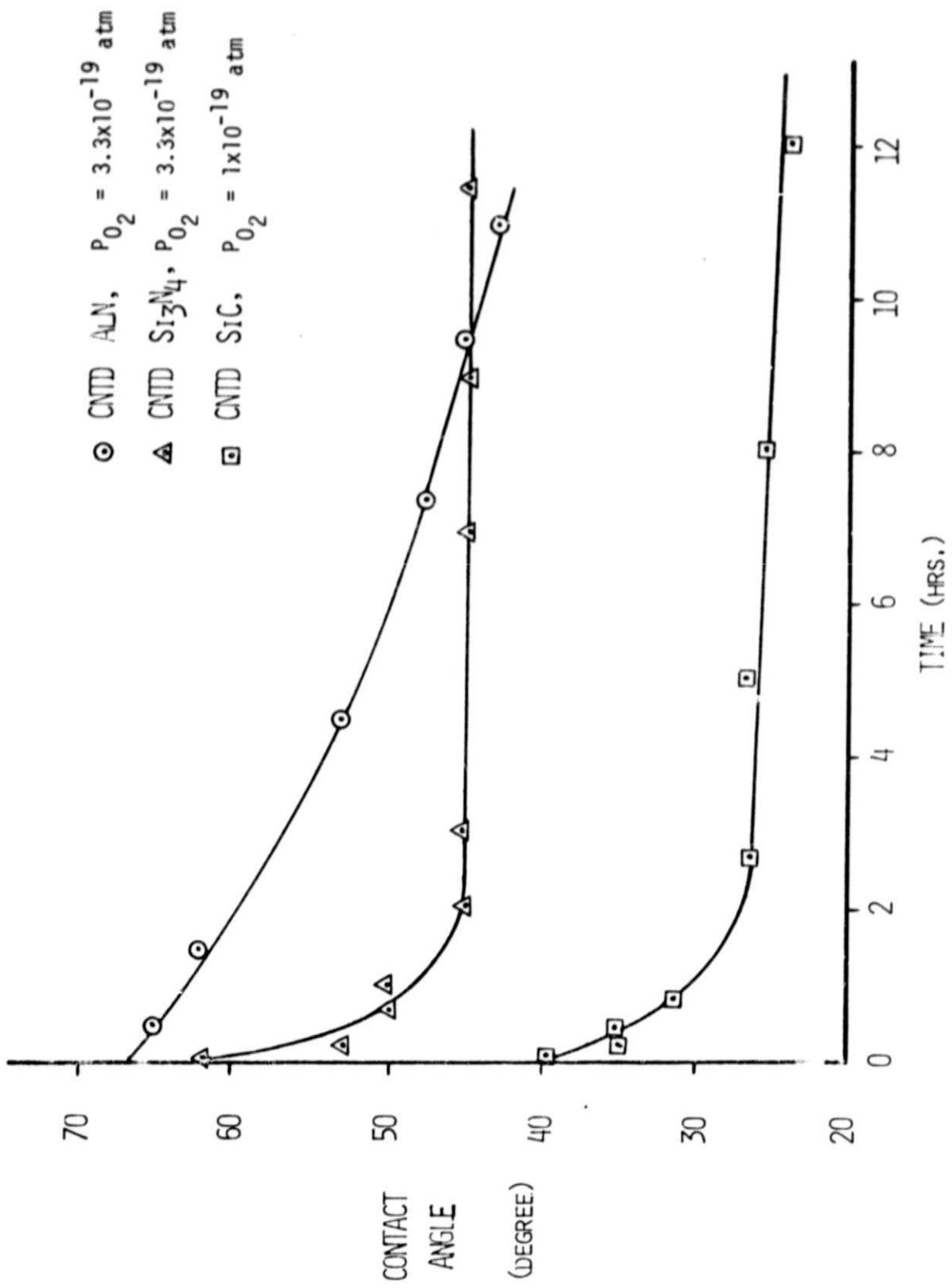


Figure 9. Time Dependence of Molten Silicon Contact Angle, CNTD Materials at  $1420^{\circ}\text{C}$ .

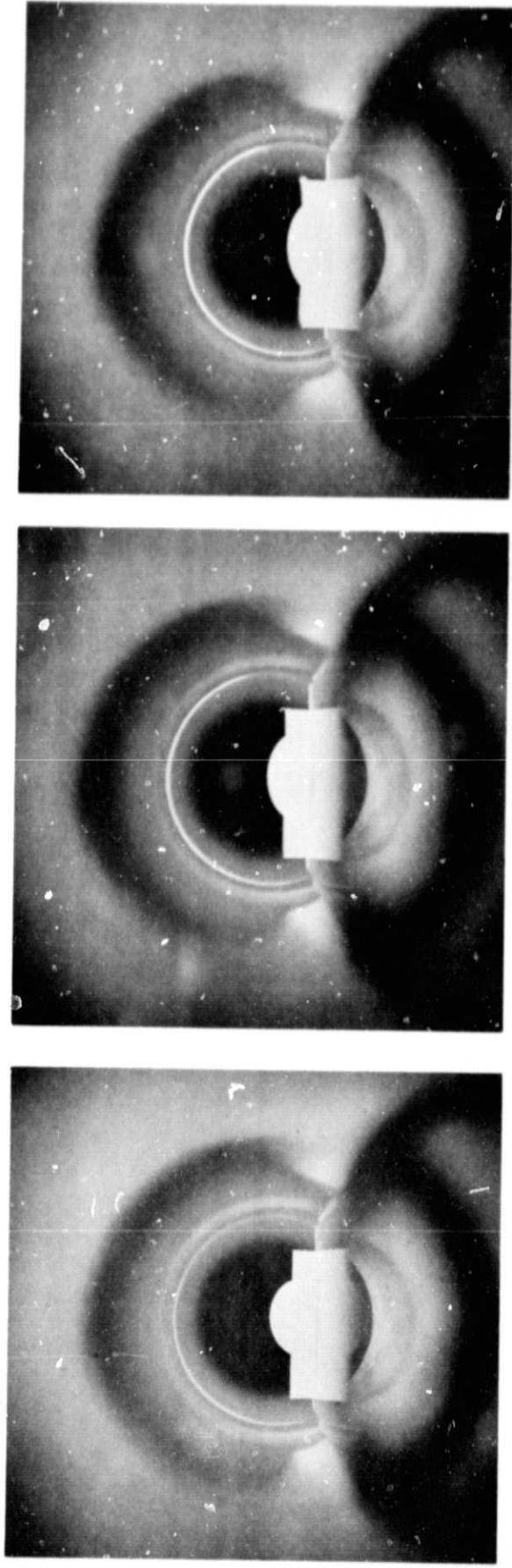


Figure 10. Growth of Whiskers During Sessile Drop Experiment on CNTD Coated AlN Specimen  
at  $1420^{\circ}\text{C}$  and  $3.3 \times 10^{-19}$  atm  $P_{\text{O}_2}$

- a) 1/2 hr. into run
- b) 4 1/4 hr. into run
- c) 9 1/4 hr. into run

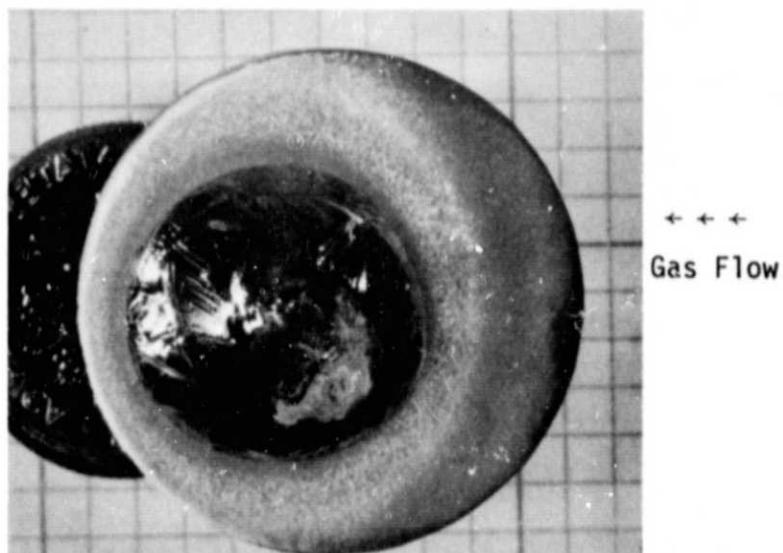
Macroscopic observation, Figure 11, reveals that these fibers are white in color and do not grow on the drop or in a thin region immediately adjacent to it and that they are most concentrated on the down stream side of the drop. The crystal system of these fibers appears to be cubic when viewed at higher magnification by SEM (Figure 12). Elemental AES analysis (Figure 13) shows that these fibers are mainly of Al, Si, C, and O, with a slight trace of S and Cl. The mechanism of the fiber growth and the properties of these material are not known at the present time.

### 3.2 CHARACTERIZATION OF POST SESSILE DROP SPECIMENS

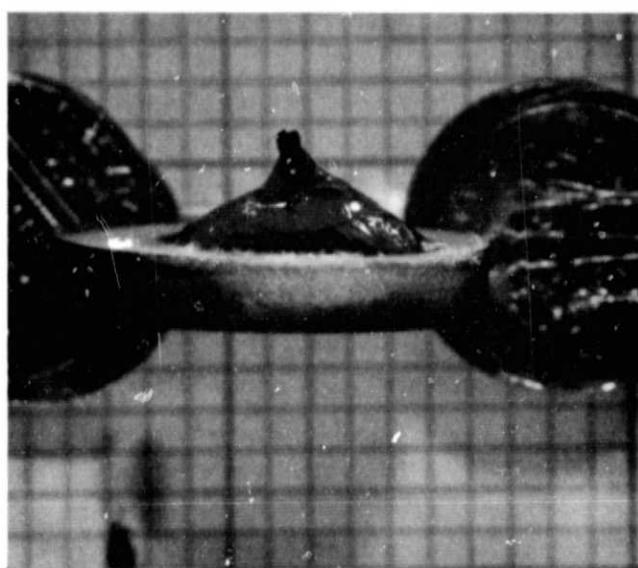
In the fourth quarterly report, optical photomicrographs of polished surfaces of molten silicon on specimens of CNTD SiC,  $\text{Si}_3\text{N}_4$  and AlN coatings on their respective hot pressed shapes were presented for the preliminary evaluation of the compatibility of these ceramic systems with molten silicon. During this current research period, the oxygen partial pressure effect and the detailed analysis on the interaction between molten silicon and specimens of CNTD AlN, SiC and  $\text{Si}_3\text{N}_4$  coatings were investigated by the analytical techniques of optical microscopy, SEM and AES. The CNTD coatings sometimes separate from the hot pressed ceramic while the post sessile drop specimens are being sectioned for analysis. Examination of these separated CNTD coatings of SiC and  $\text{Si}_3\text{N}_4$  as well as the exploration of the silicon micro-flow on hot pressed  $\text{Si}_3\text{N}_4$  were also conducted through the employment of SEM.

#### 3.2.1 Second Candidate Materials Set-CNTD Coated $\text{Si}_3\text{N}_4$

It has been described in the previous section that oxygen partial pressure has a large effect on the rate of change of the silicon contact angle on CNTD coated  $\text{Si}_3\text{N}_4$ . Lower oxygen partial pressure ambient appears to allow less interaction between molten silicon and CNTD

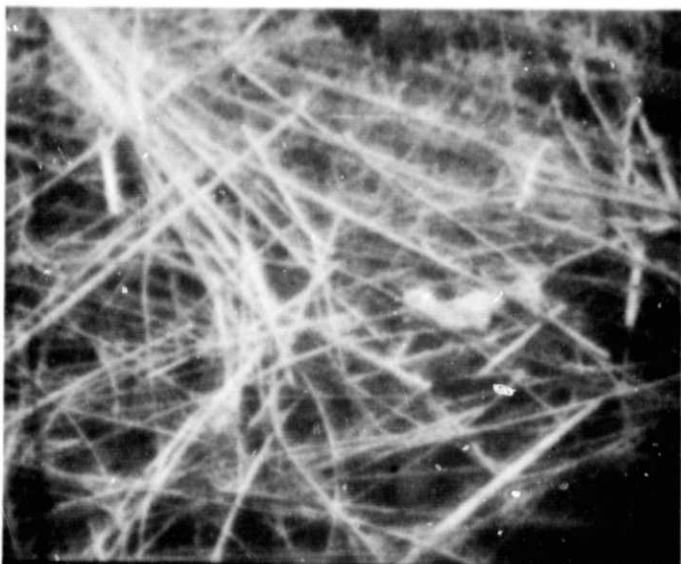


a)

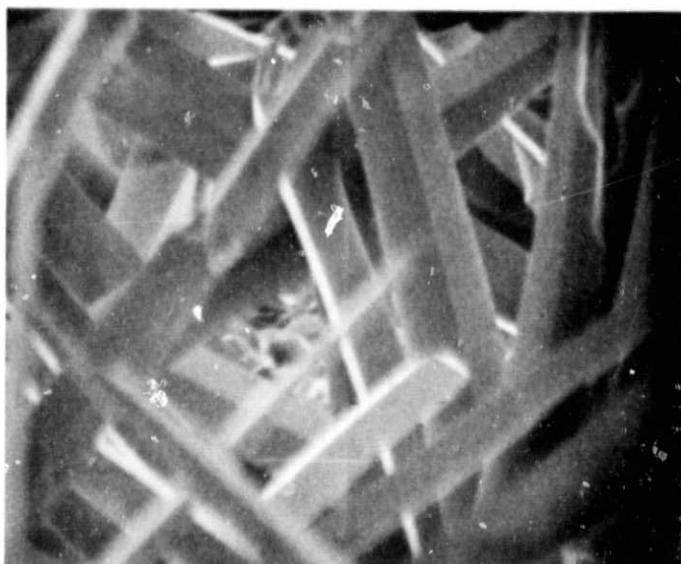


b)

Figure 11. Macroscopic Observation of Whisker Growth on CNTD AlN Coating.



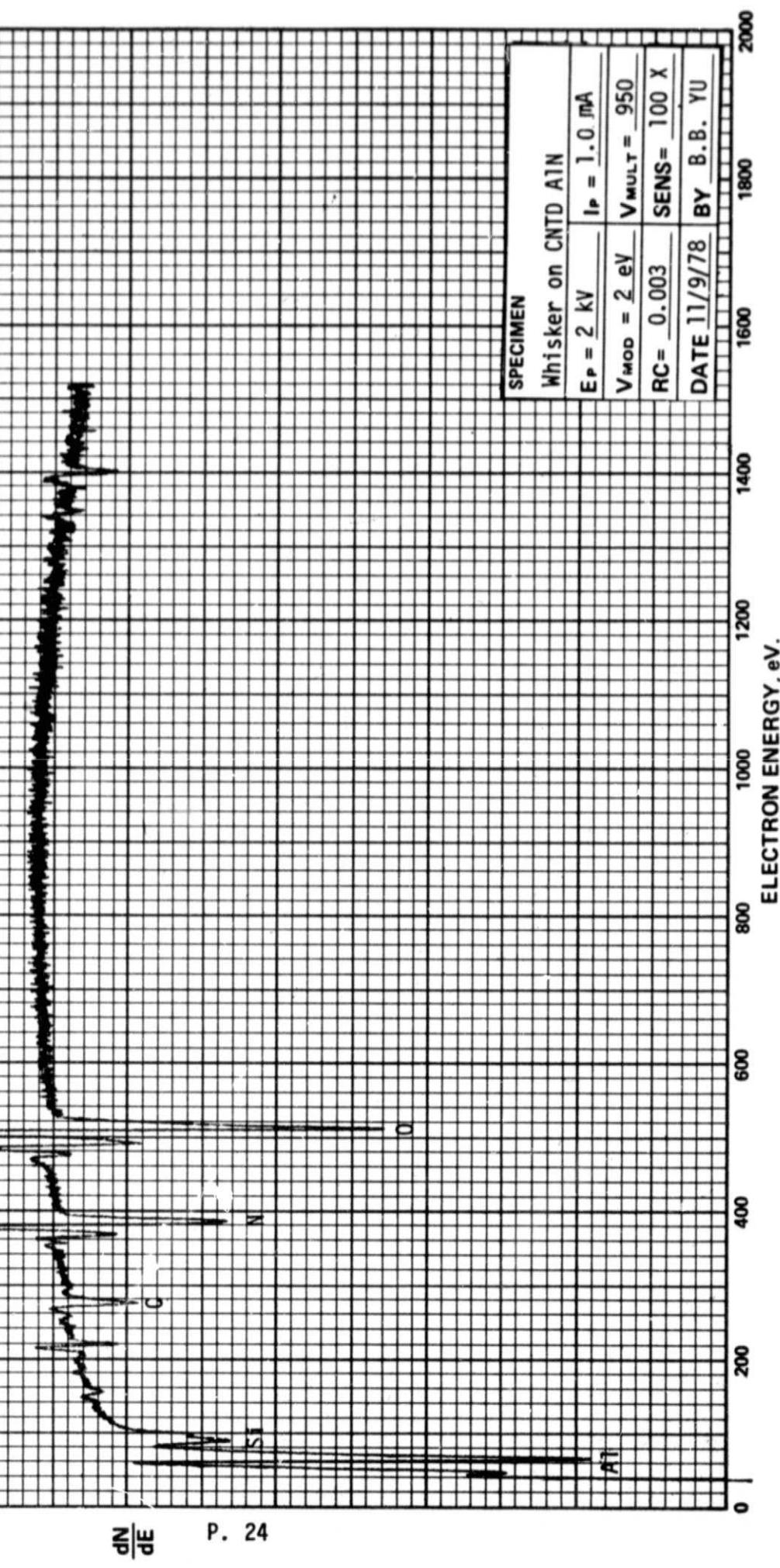
a) 250X



b) 3750X

Figure 12. SEM Examination of Whisker Growth on CNTD AlN Coating

Figure 13. AES Analysis of Whisker Growth on CNTD AlN



coated  $\text{Si}_3\text{N}_4$  indicated by the stabilization of the contact angle. Figure 14 confirms this expectation by presenting the photomicrographs of the silicon CNTD  $\text{Si}_3\text{N}_4$  interface of two specimens run at different  $P_{O_2}$  values. Pronounced dissolution-precipitation and/or preferential boundary attack have been observed near the interface after testing at  $P_{O_2} = 2.3 \times 10^{-18}$  atm for 6 hours (Figure 14-a) while a relatively clean interface is found in the specimen after 12 hours at a  $P_{O_2} = 3.3 \times 10^{-19}$  atm ambient (Figure 14-b).

An etched region and reaction zone consisting of a molten silicon infiltrated network appearing to correspond to the crack-like network observed on the polished coatings before testing were observed after prolonged high temperature testing as shown in Figure 6 and 15-A. It appears that the etched region near the peripheral part of the specimen shown on Figure 15-b is caused by thermal etching. No evidence of silicon infiltration was found outside the reaction zone. Figure 15-c shows an enlarged infiltrated river-like feature (as indicated in the central region of Figure 15-a) and vicinity inside the reaction zone. Preferential micro-wetting of the pre-existing network is responsible for this phenomenon.

An examination of the obverse side (coating to hot pressed specimen interface) of the mechanically separated CNTD coatings by SEM (Figure 16) reveals no evidence of the presence of silicon. No evidence of silicon penetration of the coating has ever been observed. The separation of the CNTD coating and  $\text{Si}_3\text{N}_4$  substrate appears to be the result of mechanical failure in the bond during the cutting process.

### 3.2.2 Uncoated Hot Pressed $\text{Si}_3\text{N}_4$

The micro-flow of molten silicon on uncoated hot pressed  $\text{Si}_3\text{N}_4$  has been described previously in section 3.1.2. Figure 17 shows

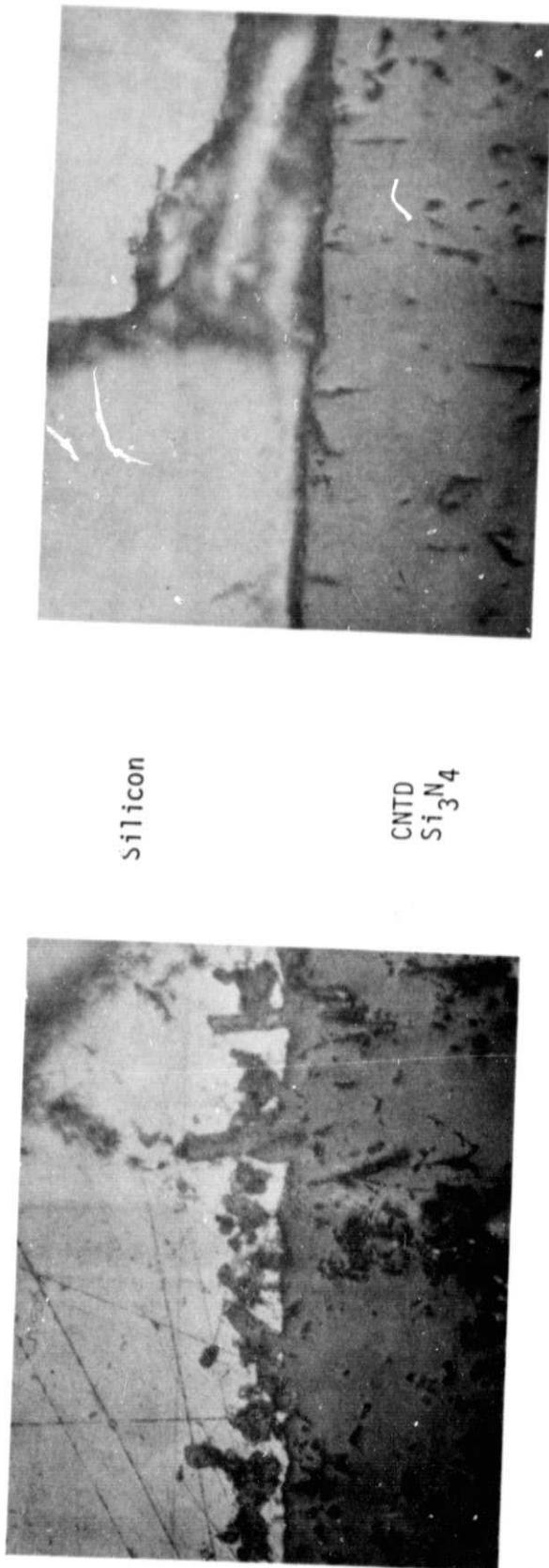


Figure 14. Oxygen Partial Pressure Effect On Interface Between Molten Silicon and CNTD  
 $\text{Si}_3\text{N}_4$  at  $1420^\circ\text{C}$ . 250X

- a)  $P_{\text{O}_2} = 2.3 \times 10^{-18} \text{ atm}$ , 6 hrs.
- b)  $P_{\text{O}_2} = 3.3 \times 10^{-19} \text{ atm}$ , 12 hrs.

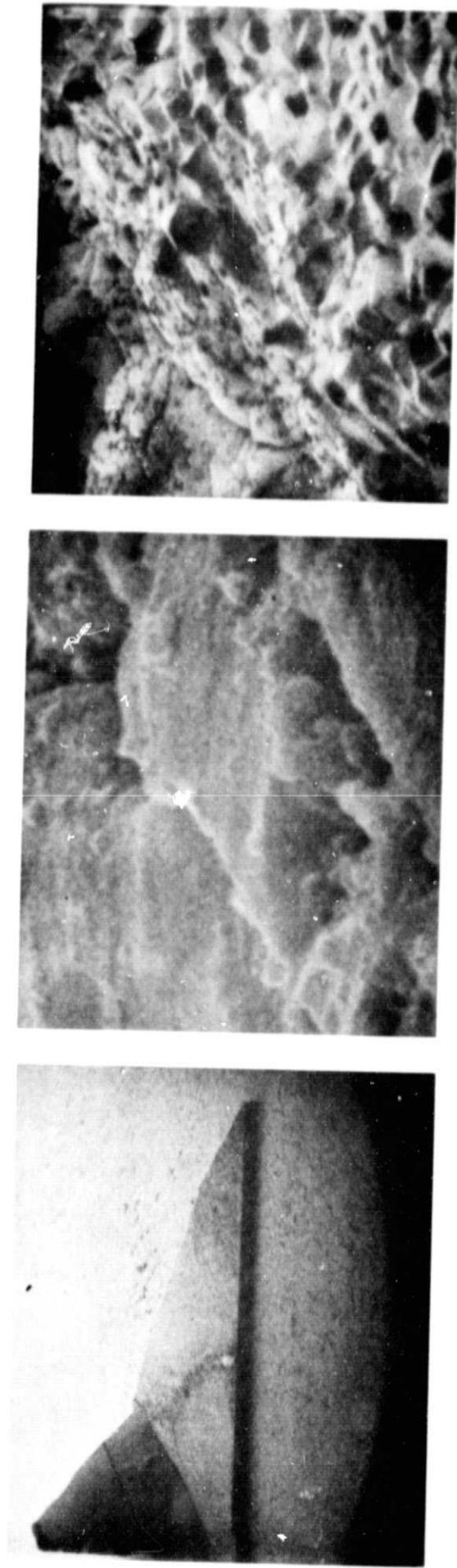
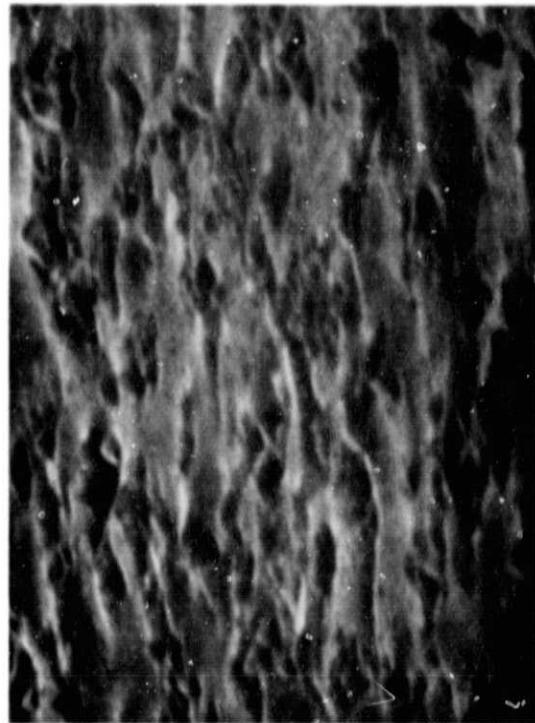


Figure 15. SEM Photographs on CNTD  $\text{Si}_3\text{N}_4$  Surface After Testing at  $1420^{\circ}\text{C}$  and  $3.3 \times 10^{-19}$  atm  $\text{P}_{\text{O}_2}$  for 12 hours.

- a) 5X, overview
- b) 375X, periphery of part, away from drop
- c) 225X, infiltrated area as in central region of a)



Figure 16. SEM Examination of the Back of a Separated CNTD  
 $\text{Si}_3\text{N}_4$  Coating. 1200X, no silicon penetration.



b)



a)

Figure 17. SEM Photographs of Sessile Drop Substrate ( $\text{Si}_3\text{N}_4$ ) Outside the Drop Area.

- a) CNTD  $\text{Si}_3\text{N}_4$ , 550X, Note etching
- b) Uncoated Hot Pressed  $\text{Si}_3\text{N}_4$ , 1000X, note silicon micro-flow.

a comparison between (a) a CNTD  $\text{Si}_3\text{N}_4$  and (b) an uncoated hot pressed  $\text{Si}_3\text{N}_4$  surface after a sessile drop run. Both photographs were taken outside of the drop area. The mechanism for silicon microflow in hot pressed  $\text{Si}_3\text{N}_4$  appears to be similar to the etching mechanism in the formation of the reaction zone on a CNTD coated  $\text{Si}_3\text{N}_4$  specimen.

### 3.2.3 First Candidate Materials Set - CNTD Coated SiC

The optical micrographs of the polished surfaces of post sessile drop test CNTD SiC coatings reported in the fourth quarterly report indicated negligible attack by molten silicon. SEM micrographs of fractured surfaces of a CNTD SiC coating after a sessile drop test at  $1420 \pm 5^\circ\text{C}$  and  $2 \times 10^{-19}$  atm  $\text{P}_{\text{O}_2}$  for 12 hours (shown in Figure 18) also reveals a very clean interface even at  $1750 \times$  which is consistent with the lower magnification observation by optical microscopy. Separation of CNTD SiC coatings from their hot pressed SiC substrates is sometimes observed as in the case of CNTD  $\text{Si}_3\text{N}_4$  coatings. Examination of the obverse side of a separated CNTD SiC coating (Figure 19) reveals the same structure under the silicon drop and on the periphery of the coating which suggests the separation is not caused by silicon attack. Failure of the mechanical bond between the coating and the substrate independent of the silicon drop on the surface is believed to cause the separation of CNTD SiC coating layer from the hot pressed SiC substrate. These separations, as in the case of  $\text{Si}_3\text{N}_4$ , occur during sectioning.

### 3.2.4 Third Candidate Material Set-CNTD Coated AlN

The molten silicon attack of CNTD AlN coated specimens under the silicon drop is found to be the most severe of all the CNTD coatings studied. The silicon penetration of CNTD AlN is more severe under the center of the sessile drop than near the periphery of the drop as shown in Figure 20.

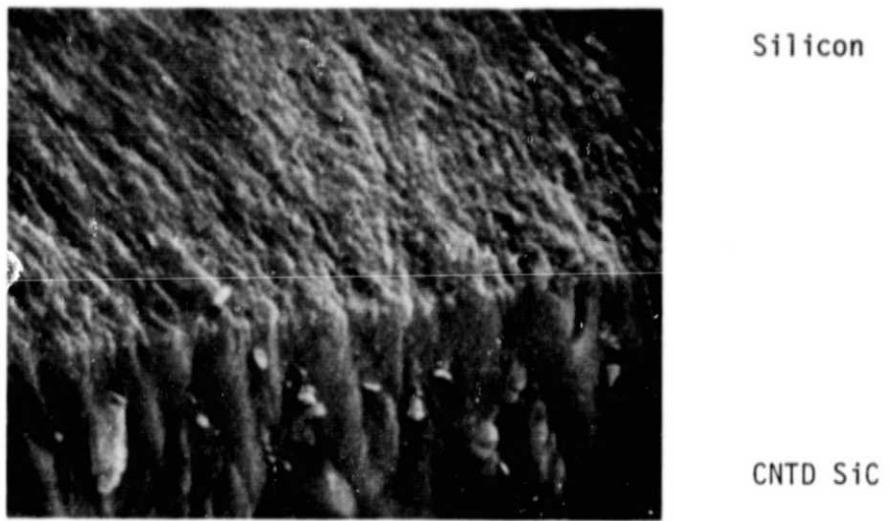
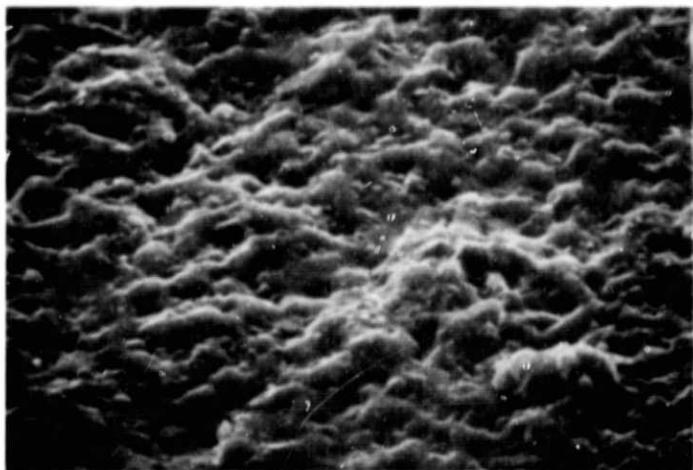
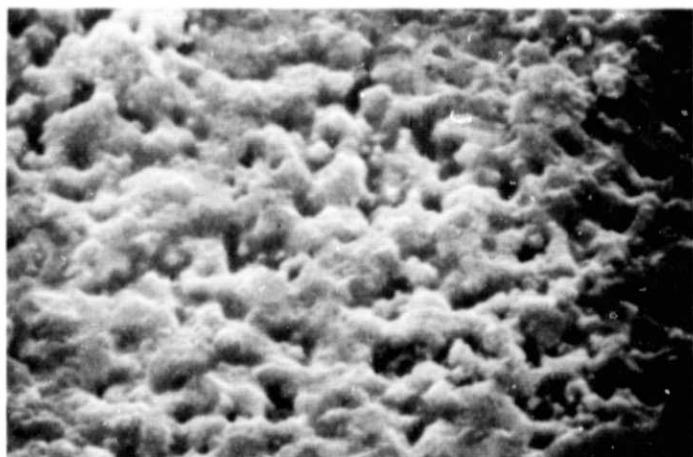


Figure 18. SEM of Fracture Through the Interface Between Silicon and CNTD SiC. After sessile drop test at  $1420^{\circ}\text{C}$  and  $2 \times 10^{-19} \text{ atm } P_{\text{O}_2}$  for 12 hrs. 1750X.



a )



b )

Figure 19. SEM of Obverse Side of a Separated CNTD SiC Coating, 1200X.

Note uniform appearance for:

- a) Directly under silicon drop
- b) Away from silicon drop area

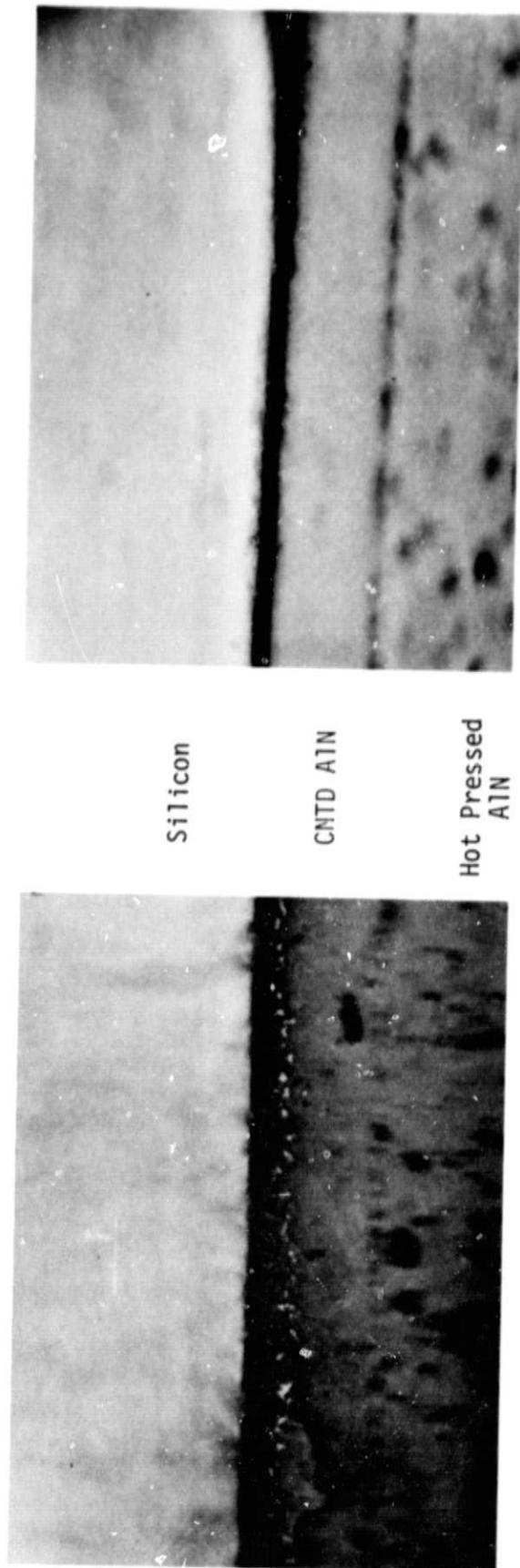


Figure 20. Optical Photomicrographs of Silicon to CNTD AlN Interface After Sessile Drop Test at  $1420^{\circ}\text{C}$  for 2 hrs., 250X

- a) Near center of silicon drop
- b) Toward edge of silicon

Auger electron spectroscopic analysis is performed on a relatively small spot size (on the order of 5 microns). When the silicon/CNTD AlN interface is examined by AES, Figure 21, near the drop center the silicon signal is absent after 17.5 min. of sputtering at a rate of  $60 \text{ \AA/min}$ . This indicates only a submicron (0.1 micron) reaction zone on a localized level. The much greater depth and the nonuniformity of the overall silicon penetration would suggest grain boundary diffusion, capillarity and/or dissolution and precipitation mechanisms dominate the coating penetration. SEM examination of the fractured surface of a post-sessile drop CNTD coated AlN specimen is also consistent with the conclusion from the optical microscopy.

#### 4. CHEMETAL EFFORTS

##### 4.1 $\text{Si}_3\text{N}_4$ CRUCIBLE COATING

Three crucibles of hot pressed  $\text{Si}_3\text{N}_4$  w/4wt% MgO were coated with CNTD  $\text{Si}_3\text{N}_4$  at Chemetal this quarter. The characterization of these coatings is discussed in section 2.3. This marks the completion of a major milestone in hardware delivery.

##### 4.2 DIE COATING

Extensive efforts were made at Chemetal during this quarter to apply CNTD  $\text{Si}_3\text{N}_4$  to one piece dies of HLM grade graphite. The graphite was chosen as a substitute for ceramic in coating development in order to limit costs. All pertinent parameters were varied, including substrate temperature, gas composition and flow rate, and in addition, fixturing was utilized which directed the reactant gas flow into the slit, however, no satisfactory method for coating the interior of the slit was developed. It was apparent that a two piece die design must be utilized.

Figure 21.a) AES on Interface of Silicon and CVD AlN Before Sputtering

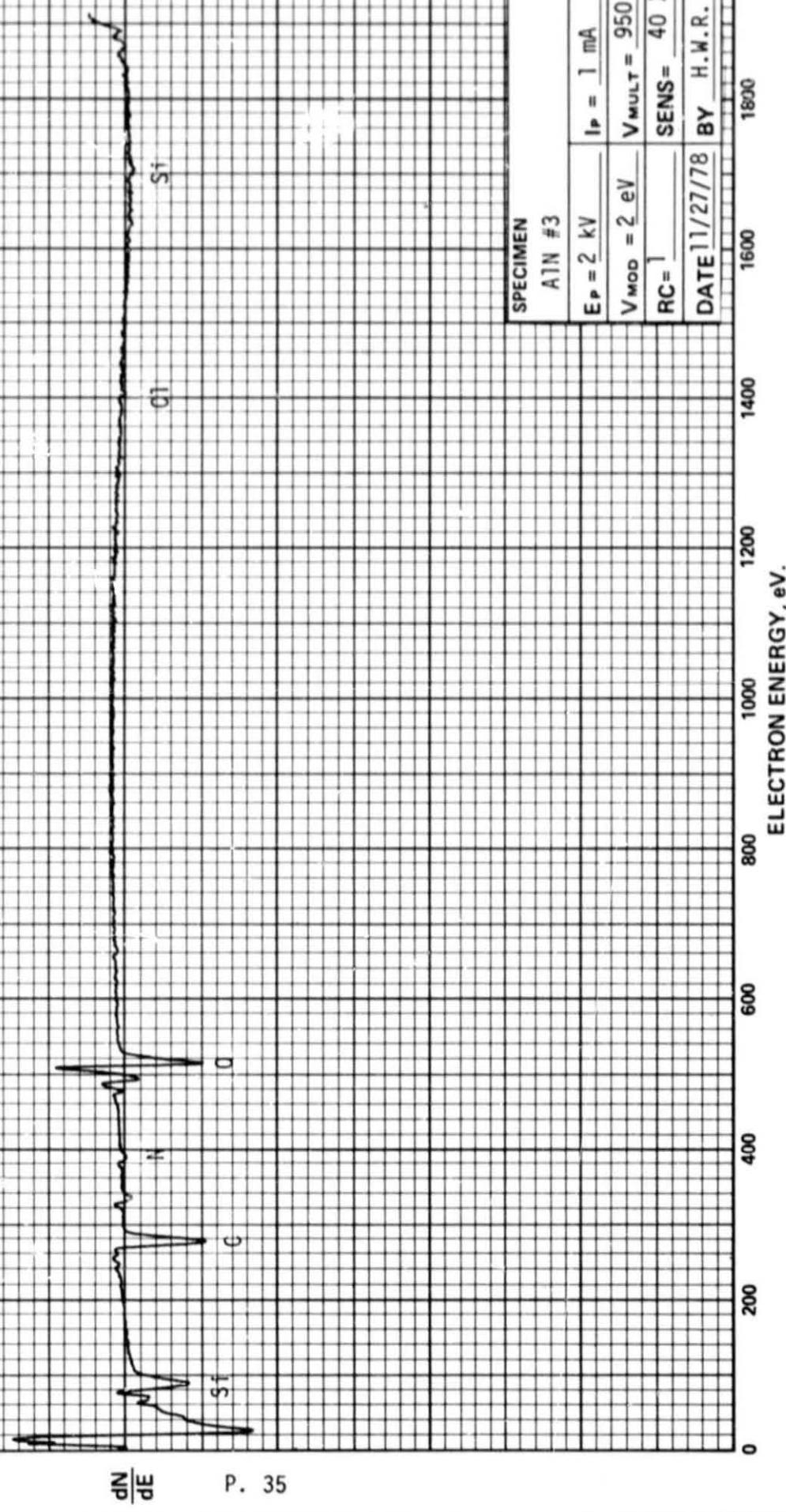
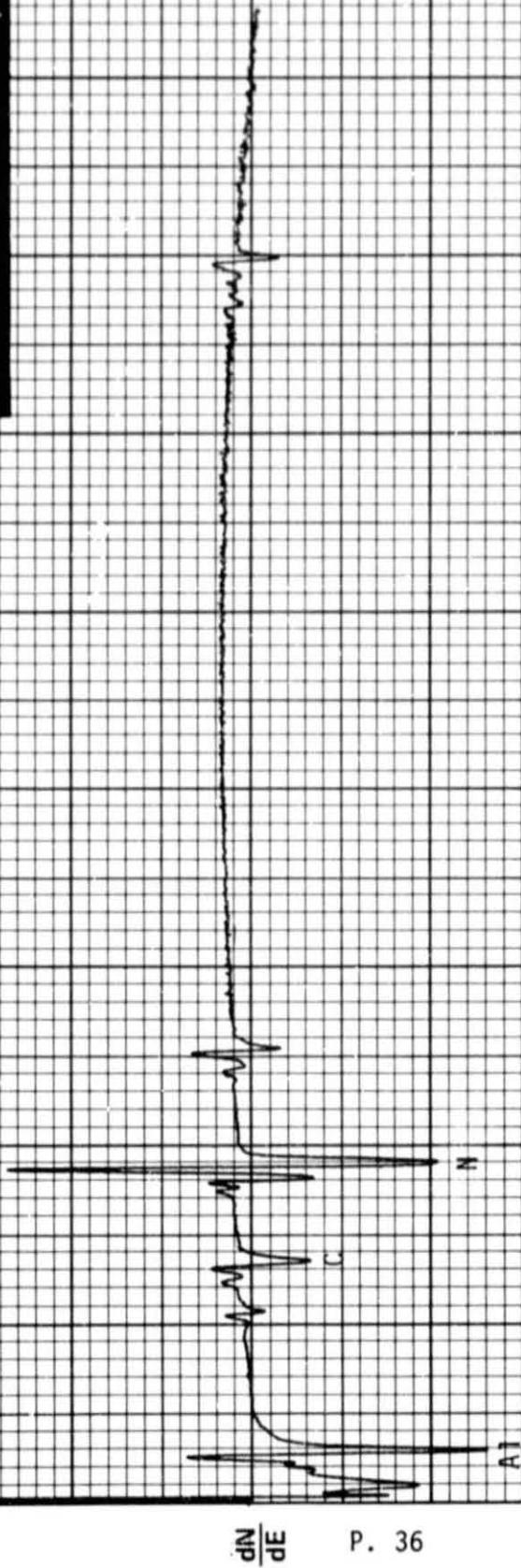


Figure 21. b) AES on Interface of Silicon and CNTD AlN After 17.5 Minutes Sputtering.



SPECIMEN  
AlN #3

$E_p = 2 \text{ kV}$	$I_p = 1 \text{ mA}$
$V_{MOD} = 2 \text{ eV}$	$V_{MULT} = 950$
RC = 1	SENS = 40 X
DATE 11/27/78	BY H.W.R.

## 5. CONCLUSIONS

The significance of the effects of oxygen partial pressure on the interaction of molten silicon and the CNTD refractory ceramic coatings is now being demonstrated. The rate of attack is diminished as the  $P_{O_2}$  is lowered as evidenced both by the increased stability of the contact angle and by post testing microscopy. The attack of the CNTD coatings by molten silicon is most severe near the center of the drop which suggests the possibility of an adsorbed oxygen influence.

Higher temperatures and longer run times continue to verify the relative stability of the CNTD materials in contact with molten silicon.

The necessity of utilizing a two piece die design is readily apparent.

## 6. PROJECTED ACTIVITIES FOR THE SIXTH QUARTER

Efforts at MRL will be directed toward hot pressing and grinding the required ceramic die blanks for the two piece die design. A portion of the one piece dies currently on hand may be convertible to the two piece design by grinding away one half and forming the required spacing runners. Engineering evaluations will be directed toward projected fabrication costs for production of crucibles and dies developed in this effort.

Efforts at UMR will be directed toward a more complete understanding of the role of oxygen in influencing the reaction between molten silicon and the CNTD materials. The possibility of adsorbed oxygen remaining in the region near the center of the drop due to an insufficient hydrogen gettering while the silicon cube heats up in contact with the specimen will be explored.

At Chemetal the recently delivered SiC (w/1wt% B) hot pressed crucibles will be coated with CNTD SiC.  $\text{Si}_3\text{N}_4$  and SiC die blanks will be coated as they are made available by MRL.